



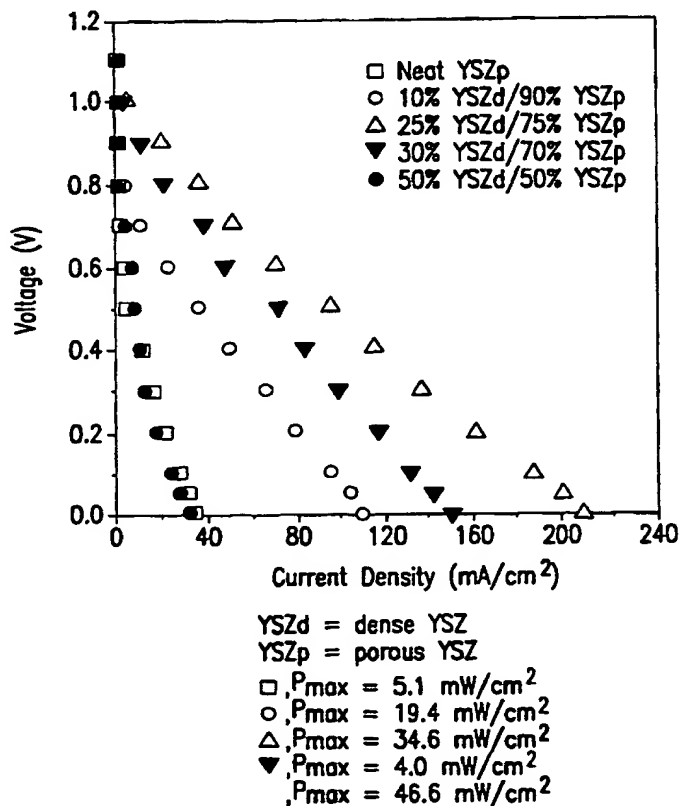
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : H01M 8/12		(11) International Publication Number: WO 00/52780
A1		(43) International Publication Date: 8 September 2000 (08.09.00)
(21) International Application Number: PCT/US00/05735 (22) International Filing Date: 3 March 2000 (03.03.00) (30) Priority Data: 09/261,324 3 March 1999 (03.03.99) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/261,324 (CIP) Filed on 3 March 1999 (03.03.99) (71) Applicant (for all designated States except US): GAS RESEARCH INSTITUTE [US/US]; 8600 West Bryn Mawr Avenue, Chicago, IL 60631 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): GORTE, Raymond, J. [US/US]; 512 Broad Acres Road, Narberth, PA 19072 (US). VOHS, John, M. [US/US]; 45 Sawgrass Lane, Newtown Square, PA 19073 (US). CRACIUN, Radu [US/US]; 3426 Bailey Creek Cove, South Collierville, TN 38109 (US).		(74) Agents: FEJER, Mark, E. et al.; Pauley Petersen Kinne & Fejer, Suite 365, 2800 West Higgins Road, Hoffman Estates, IL 60195 (US). (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

(57) Abstract

A method for preparation of an anode for a solid oxide fuel cell in which a plurality of zircon fibers are mixed with a yttria-stabilized zirconia (YSZ) powder, forming a fiber/powder mixture. The fiber/powder mixture is formed into a porous YSZ layer and calcined. The calcined porous YSZ layer is then impregnated with a metal-containing salt solution. Preferred metals are Cu and Ni. An anode and a method for manufacturing a fuel cell containing such anode is also disclosed. Such anode is particularly performant when the fuel cell is fed with dry hydrocarbons, in absence or low content of steam.



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METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to a method for preparation of anodes for use in solid oxide fuel cells. More particularly, this invention relates to a method for preparation of an anode for a solid oxide fuel cell in which metals and catalytic materials employed in such anodes are added in a separate step compared to conventional methods of anode preparation.

Description of Prior Art

10 Solid oxide fuel cells have grown in recognition as a viable high temperature fuel cell technology. There is no liquid electrolyte with its attending metal corrosion and electrolyte management problems. Rather, the electrolyte of the cells is made primarily from solid ceramic materials so as to survive the high temperature environment. The operating temperature of greater than about 600°C allows internal reforming, promotes rapid kinetics
15 with non-precious materials, and produces high quality by-product heat for cogeneration or for use in a bottoming cycle. The high temperature of the solid oxide fuel cell, however, places stringent requirements on its materials. Because of the high operating temperatures of conventional solid oxide fuel cells (approximately 1000°C), the materials used in the cell components are limited by chemical stability in oxidizing and reducing environments,
20 chemical stability of contacting materials, conductivity, and thermomechanical compatibility.

 The most common anode materials for solid oxide fuel cells are nickel (Ni)-cermets prepared by high-temperature calcination of NiO and yttria-stabilized zirconia (YSZ) powders. High-temperature calcination is essential in order to obtain the necessary ionic conductivity in the YSZ. These Ni-cermets perform well for hydrogen (H₂) fuels and
25 allow internal steam reforming of hydrocarbons if there is sufficient water in the feed to the anode. Because Ni catalyzes the formation of graphite fibers in dry methane, it is necessary to operate anodes at steam/methane ratios greater than 3. However, there are significant advantages to be gained by operating under dry conditions. Progress in this area has been made using an entirely different type of anode, either based on ceria (See Eguchi, K, et al.,
30 Solid State Ionics, 52, 165 (1992); Mogensen, G., Journal of the Electrochemical Society,

141, 2122 (1994); and Putna, E.S., et al., Langmuir, 11 4832 (1995)) or perovskite anodes (See Baker, R.T., et al., Solid State Ionics, 72, 328 (1994); Asano, K., et al., Journal of the Electrochemical Society, 142, 3241 (1995); and Hiei, Y., et al., Solid State Ionics, 86-88, 1267 (1996)). These oxides do not, however, provide sufficient electronic conductivity.

5 Replacement of Ni for other metals, including Co (See Sammes, N.M., et al., Journal of Materials Science, 31, 6060 (1996)), Fe (See Bartholomew, C.H., Catalysis Review-Scientific Engineering, 24, 67 (1982)), Ag or Mn (See Kawada, T., et al., Solid State Ionics, 53-56, 418 (1992)) has been considered; however, with the possible exception of Ag, these are likely to react with hydrocarbons in a way similar to that of Ni. Substitution of Ni with

10 Cu would also be promising but for the fact that CuO melts at the calcination temperatures which are necessary for establishing the YSZ matrix in the anodes.

It is also well known that the addition of ceria to the anode improves performance. However, the high-temperature calcination utilized in conventional anode preparation causes ceria to react with YSZ, as a result of which performance is not enhanced

15 to the extent which could be possible if formation of ceria-zirconia did not occur.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a method for preparation of solid oxide fuel cell anodes which enables the use of lower melting temperature materials than employed by conventional solid oxide fuel cell anodes.

20 It is another object of this invention to provide a process for solid oxide fuel cell anode preparation which enables efficient operation using dry natural gas as a fuel.

It is another object of this invention to provide a method for generation of electricity by direct oxidation of hydrocarbons and other carbonaceous fuels.

25 It is yet another object of this invention to provide a method for a solid oxide fuel cell anode preparation which enables the use of ceria to improve anode performance while avoiding the formation of ceria-zirconia which reduces the extent of performance enhancement in conventional solid oxide fuel cell anodes.

These and other objects of this invention are addressed by a method for preparation of an anode for a solid oxide fuel cell in which a plurality of zircon fibers or

30 other porous matrix material is mixed with a yttria-stabilized-zirconia (YSZ) powder, thereby

forming a fiber/powder mixture. The fiber/powder mixture is then formed into a porous YSZ layer and calcined. The calcined porous YSZ layer is then impregnated with a metal-containing salt solution. Accordingly, contrary to conventional methods for solid oxide fuel cell anode preparation, the method of this invention results in a YSZ layer which remains highly porous following high-temperature calcination to which any suitable metal, including Cu and Ni is then added by impregnation of the salt solution, after the high temperature calcination of the YSZ layer. In addition to enabling the use of metals whose oxides have a low melting temperature, the method of this invention also allows catalytic materials, such as ceria and/or palladium (Pd) to be added in controlled amounts in a separate step.

Cells prepared in accordance with the method of this invention with Ni perform in a very similar manner to those cells prepared using conventional means. With Cu used in place of Ni, there is a possibility of oxidizing hydrocarbons (C_xH_y) and other carbonaceous fuels ($C_xH_yO_z$) such as methanol, ethanol, propanol and the like directly, particularly since Cu is inert in dry methane. Even without direct conversion, the Cu-YSZ anode allows the use of dryer gases (partially reformed methane), because Cu is inert to methane. To convert methane, it is necessary to add a catalytic component. Ceria, particularly when doped with noble metals like Pd, Pt, or Rh, is active for this process.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

Fig. 1 is a diagram showing the I-V relationship for cells at 800°C in H_2 prepared by impregnating porous YSZ with 40% Cu in accordance with one embodiment of this invention;

Figs. 2A, 2B, and 2C show SEM micrographs for conventional Ni-cermet prepared from NiO and dense yttria-stabilized zirconia, designated as YSZd, neat porous yttria-stabilized zirconia designated as YSZp, and Cu-cermet prepared from 25% YSZd impregnated with 40% Cu, respectively;

Fig. 3 is a diagram showing the I-V relationship for cells at 800°C in H_2 prepared by impregnating porous YSZ (25% YSZd) with varying amounts of Cu;

Fig. 4 is a diagram showing the I-V relationship for cells at 800°C in H₂ with a conventional Ni-cermet anode, a Ni-cermet anode prepared from porous YSZ (25% YSZd), and Cu-cermet prepared from porous YSZ (25% YSZd);

5 Fig. 5 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZp;

Fig. 6 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZ mixture;

Fig. 7 is a diagram showing current density as a function of time for Ni- and Cu-based cells during switching of fuels from dry H₂ to dry CH₄ and back; and

10 Fig. 8 is a diagram showing the I-V relationship for Cu-based cells with methane.

DESCRIPTION OF PREFERRED EMBODIMENTS

As previously stated, conventional solid oxide fuel cells are unable to operate efficiently in dry natural gas. This is due to the fact that they typically have Ni-cermet
15 anodes which are prepared by high-temperature calcination of powders consisting of NiO and yttria-stabilized zirconia. High-temperature calcination is essential in order to obtain the necessary ionic conductivity in the YSZ. Under the reducing conditions of operation, NiO is reduced to the metal and provides electronic conductivity. However, in dry methane, Ni tends to form graphite fibers which quickly deactivate the system. Ni can be replaced by Fe
20 or Co, but these metals suffer from similar problems. We have developed a method for preparation of an anode for a solid oxide fuel cell which allows the addition of the electron-conducting metal, including metals like Cu, for which the oxide melts at low temperature, in a manner which does not require the high-temperature calcination of conventional methods. In addition, catalytic and ion-transfer components, such as ceria, lanthana,
25 manganese, and precious metals can also be added without further, high-temperature treatment.

In accordance with the method of this invention, a plurality of zircon fibers or other porous matrix material is mixed with a yttria-stabilized-zirconia powder, forming a fiber/powder mixture. The fiber/powder mixture is formed into a porous YSZ layer and
30 calcined. After calcination, the porous YSZ layer is impregnated with a metal-containing salt

solution. In accordance with one preferred embodiment of this invention, the metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

In accordance with one preferred embodiment of this invention, the fiber/powder mixture is made into a slurry with glycerol and then applied to the anode side of the dense YSZ electrolyte of a solid oxide fuel cell. In accordance with another preferred embodiment, the powdered fibers are added to a tapecast which can be included as a layer in a composite with a second layer which will give dense YSZ. The system is then calcined at a suitable temperature, for example 1550°C, for two hours. After addition of the cathode to the cathode side of the YSZ electrolyte, the porous YSZ layer on the anode side is impregnated with aqueous solutions of $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ to bring the metal content of the anode to at least 35% by weight metal, after which the anode is calcined at 950°C for two hours. It is very important either to mix a normal YSZ powder (about 20% by weight) with the zircon fibers in the original glycerol slurry, or to add ceria or YSZ to the porous YSZ layer so as to provide sufficient oxide in the anode for ionic conductivity. Ceria in accordance with one embodiment of this invention is added using an aqueous solution of $\text{Ce}(\text{NO}_3)_3$ to the porous anode, after addition of the metal. After drying, the anode is again calcined to 900°C to form the oxide or ceria. In accordance with a particularly preferred embodiment of this invention, ceria constitutes in the range of about 5% to about 40% by weight of the porous YSZ layer.

Example

Yttria-stabilized zirconia (8% Y_2O_3 , Tosoh TZ-8Y, denoted as YSZd) was used for the fabrication of the electrolyte and conventionally prepared anode for a solid oxide fuel cell. The electrolyte wafers were formed from YSZd by tapecasting, followed by calcination to 1400°C for two hours. The cathodes were formed from a 50% by weight physical mixture of Sr-LaMnO_3 and YSZd powders, pasted onto the electrolyte with glycerol, and then calcined at 1250°C for two hours. The conventional, Ni-cermet anode was prepared using a 50% by weight physical mixture of NiO and YSZd, followed by calcination to 900°C. This Ni-cermet was pasted onto the electrolyte using glycerol and calcined to 1400°C.

In accordance with the method of this invention for preparation of an anode for a solid oxide fuel cell, a porous YSZ layer was prepared from physical mixtures of zircon fibers (YSZ, 75% porosity, with less than about 0.3% Si, Zircar Products, Inc., denoted as YSZp) and YSZd. The physical mixture (denoted as YSZm) was pasted onto the electrolyte
5 using glycerol and calcined to 1550°C for two hours. After addition of the cathode, the porous YSZ layer was impregnated with aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ (Fisher Scientific) or $\text{Ni}(\text{NO}_3)_2$ (Aldrich) followed by calcination at 950°C for two hours, at a Cu (or Ni) content of 40% by weight.

A sample doped with ceria was prepared by adding ceria in an amount of
10 about 5 to about 40 weight percent of the anode material, to the anode by impregnation using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) followed by calcination to 950°C. The fraction of YSZd used in the anode and the metal content of the anode were varied.

Pt electrodes were attached to both anodes and cathodes using a Pt ink (Engelhard, A4338), followed by calcination at 950°C for thirty minutes. The cells were
15 sealed into Al_2O_3 tubes using quartz powder in polyvinyl solutions. They were then conditioned in H_2 for three to four hours at 950°C. The performance of the cells was measured using flowing H_2 at 1 atmosphere at the anode, and the cathode was open to air.

SEM images were obtained using a JEOL 6300 microscope equipped with an X-ray analyzer for EDX analysis. Samples were deposited onto carbon tape and coated with
20 a gold film before analysis. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.541838 \text{ \AA}$). The mean crystallite size (\bar{d}) of YSZ particles was determined from XRD line-broadening measurements using the Scherrer equation.

Fig. 1 shows the performance for series of cells prepared with Cu-cermet
25 anodes at 800°C. In this series, the Cu content was maintained at approximately 40% by weight, but the fraction of non-porous YSZd was varied. Performance for the pure zircon fibers (neat YSZp) was poor, giving a maximum power density of only 5.1 mW/cm² and a maximum current density of 35 mA/cm². Adding YSZd to the layer improved the performance significantly, with the best performance being achieved at about 25% by weight
30 YSZd. The maximum power density for this cell was nearly 50 mW/cm², with a maximum

current density of 210 mA/cm². Increasing the fraction of YSZd in the layer led to poorer performance. The results in Fig. 1 demonstrate the importance of maintaining the proper structure of the YSZ in the anode as well as the possibility of a deleterious effect of Si in the zircon fibers.

5 Figs. 2A, 2B, and 2C show SEM pictures of several representative samples of anodes taken for the purpose of investigating their morphologies. Fig. 2A is a micrograph of the conventional Ni-cermet taken at a magnification of 5000x. Shown is a dense film made up of about 1-micron particles. Before exposure to H₂ (the fuel atmosphere), EDX analysis and XRD patterns show the presence of NiO particles as a physical mixture with the
10 YSZ ($\bar{d} = 28.5$ nm). After exposure to H₂ at 950°-800°C (reducing atmosphere), NiO is reduced to Ni metal ($\bar{d} = 26$ nm), determining a small porosity (about 20%) to the compact NiO-YSZ material. The micrographs of the neat zircon fibers, shown in Fig. 2B at 1500x after heating to 1550°C, show rods, roughly 20 microns long and 5 microns in diameter. The film remains highly porous, about 70% void, but contact between the rods appears to be
15 poorer. Finally, the film formed by adding 25% by weight YSZd and Cu in accordance with the method of this invention is shown in Fig. 2C. The structure remains open due to the rod-like fibers. Even with the addition of non-porous YSZd and significant amounts of Cu, the film remains highly porous. Before H₂ exposure, small crystallites of CuO ($\bar{d} = 12.3$ nm) were formed on the YSZm material. After H₂ exposure at 950°C, Cu metal particles ($\bar{d} = 34$
20 nm) are formed, as was observed in the Ni-cermet case.

The effect of changing the Cu content in the anode for the YSZm made from 25% by weight YSZd is shown in Fig. 3. As can be seen, there is a definite improvement in cell performance observed with increases in Cu from about 20% to about 50% by weight Cu.

Fig. 4 shows a comparison of results for a Ni-cermet anode prepared by
25 conventional methods, a Ni-cermet with 40% Ni prepared from YSZm in accordance with one embodiment of this invention and a Cu-cermet with 40% by weight Cu prepared from YSZm in accordance with one embodiment of this invention. The results for all three cells are virtually identical, with maximum power densities between 45 and 50 mW/cm². The similarity in performance suggests that the performance of these three cells is limited by the
30 electrolyte and cathodes and not the anodes. In addition, because the catalytic properties of

Ni and Cu are very different, with H_2 dissociation occurring much more readily on Ni, this suggests that the catalytic properties of the metals are not crucial in this application with H_2 fuels. Rather Ni and Cu are primarily electronic conductors in this case.

Figs. 5 and 6 show the typical doping effect of ceria on Cu/YSZp and Cu/YSZm prepared using the method of this invention. The data for these cells shows that the power densities increased significantly with the addition of ceria. For 40% by weight ceria addition to Cu/YSZp and Cu/YSZm, the best results achieved were 151.2 mW/cm^2 and 146.4 mW/cm^2 , which compared to 5.1 mW/cm^2 and 46.6 mW/cm^2 obtained in the same cells without ceria. The measured current density on CeO_2 /Cu/YSZp was much higher than neat Cu/YSZp according to ceria contents. However, the current density does not increase over 20% by weight ceria on Cu/YSZm. In such ceria content range, there is a limit to the improvement of cell performance obtained.

The effect of adding ceria and Pd, using dry methane as a fuel is shown in Figs. 7 and 8. Before discussing the I-V curves, it is important to address the stability issues. As expected, the Ni-YSZ anode prepared in accordance with the method of this invention deactivated rapidly. While we did observe currents at 800°C , they decreased rapidly over the period of a few minutes with the formation of a carbonaceous residue. This is shown in Fig. 7, which shows the current density for a Ni/ CeO_2 /YSZ (open circles) at a cell voltage of 0.5 volts with switching of fuels from dry H_2 to dry CH_4 and back. The cell with a Ni/ CeO_2 /YSZ anode deactivated rapidly. Visual inspection showed the presence of carbon. By contrast, the Cu/ CeO_2 /YSZ cells were entirely stable. Following exposure to dry CH_4 for up to three days, we observed no evidence of decreased performance or carbon formation.

The performance of the Cu-based cells with methane is shown in Fig. 8. For the Cu-YSZ anode, the OCV was only about 0.5 volts and the power density was minimal. Addition of ceria led to a dramatic improvement, as did the addition of Pd. However, the maximum power density with methane is still much lower than with hydrogen, about 80 mW/cm^2 compared to 165 mW/cm^2 . This difference between methane and hydrogen is lowered by working at higher temperatures. At 900°C , the maximum power density achieved with this cell was about 230 mW/cm^2 with H_2 and 160 mW/cm^2 with CH_4 . This suggests that

the catalytic reaction is at least partly limiting the reaction with methane, but that reasonable performance can be achieved with dry methane if a catalytic component is added.

As demonstrated hereinabove, we have developed an entirely new method for fabricating anodes which allows the addition of metals and/or catalytic materials after the high-temperature calcination step. We have demonstrated that we can achieve similar performance levels with Cu-cermets as can be achieved with Ni-cermets. And, we have found that ceria plays an important role in anode design.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

WE CLAIM:

1. A method for preparation of an anode for a solid oxide fuel cell comprising the steps of:

mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;
forming said porous matrix material/powder mixture into a porous YSZ layer;
calcining said porous YSZ layer; and
impregnating said porous YSZ layer with a metal-containing salt solution.

2. A method in accordance with Claim 1, wherein said porous matrix material comprises a plurality of zircon fibers.

3. A method in accordance with Claim 1, wherein said metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

4. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is mixed with glycerol and applied to an anode side of a YSZ electrolyte, forming said porous YSZ layer on said anode side of YSZ electrolyte.

5. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is added to a tapecast and said tapecast is deposited onto an anode side of a YSZ electrolyte layer, forming said porous YSZ layer on said anode side of YSZ electrolyte.

6. A method in accordance with Claim 5, wherein a cathode is applied to a cathode side of said YSZ electrolyte layer after said calcining of said porous YSZ layer.

7. A method in accordance with Claim 1, wherein a metal content of said porous YSZ layer is at least about 35% by weight of said porous YSZ layer.

8. A method in accordance with Claim 1, wherein said impregnated porous YSZ layer is calcined.

9. A method in accordance with Claim 1, wherein said porous YSZ layer is impregnated with ceria.

10. A method in accordance with Claim 9, wherein said ceria constitutes in a range of about 5% to about 40% by weight of said porous YSZ layer.

11. A method for producing a solid oxide fuel cell comprising the steps of:

mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;

mixing said porous matrix material/powder mixture with glycerol, forming a slurry;

applying said slurry to an anode-facing face of a dense YSZ electrolyte layer, forming a porous anode layer/electrolyte layer assembly;

calcining said porous anode layer/electrolyte layer assembly;

applying a cathode layer to a cathode-facing face of said electrolyte layer, forming a fuel cell assembly;

impregnating said porous anode layer with a metal-containing salt solution; and

calcining said impregnated porous anode layer.

12. A method in accordance with Claim 11, wherein said metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

13. A method in accordance with Claim 12, wherein a metal content of said calcined impregnated porous anode layer is at least about 35% by weight of said calcined impregnated porous anode layer.

5 14. A method in accordance with Claim 11, wherein said porous matrix material comprises a plurality of zircon fibers.

15 15. In a solid oxide fuel cell comprising an anode electrode, a cathode electrode and an electrolyte disposed between said anode electrode and said cathode electrode, the improvement comprising:

said anode electrode comprising a porous YSZ layer and an electron-conducting metal having an oxide form which melts at a temperature less than about 1550°C.

15 16. A solid oxide fuel cell in accordance with Claim 15, wherein said electron-conducting metal is Cu.

17. A solid oxide fuel cell in accordance with Claim 15, wherein said anode electrode further comprises ceria.

20 18. A solid oxide fuel cell in accordance with Claim 15, wherein a metal content of said anode electrode is at least about 35% by weight of said porous YSZ layer.

25 19. A solid oxide fuel cell in accordance with Claim 17, wherein a ceria content of said anode electrode is in a range of about 5% to 40% by weight of said porous YSZ layer.

20. A method for generating electricity comprising the steps of:

introducing at least one of a hydrocarbon and a carbonaceous fuel directly into an anode side of a solid oxide fuel cell comprising an anode electrode comprising a porous YSZ layer and an electron-conducting metal having an oxide form which melts at a temperature less than about 1550°C, a cathode electrode and an electrolyte disposed between said anode electrode and said cathode electrode;

introducing an oxidant into a cathode side of said solid oxide fuel cell; and

directly oxidizing said at least one of said hydrocarbon and said carbonaceous fuel in said solid oxide fuel cell, resulting in generation of electricity.

21. A method in accordance with Claim 20, wherein said hydrocarbon comprises at least two carbon atoms.

22. A method in accordance with Claim 20, wherein said electron-conducting metal is Cu.

23. A method in accordance with Claim 20, wherein said anode electrode further comprises ceria.

24. A method in accordance with Claim 20, wherein said carbonaceous fuel is an alcohol.

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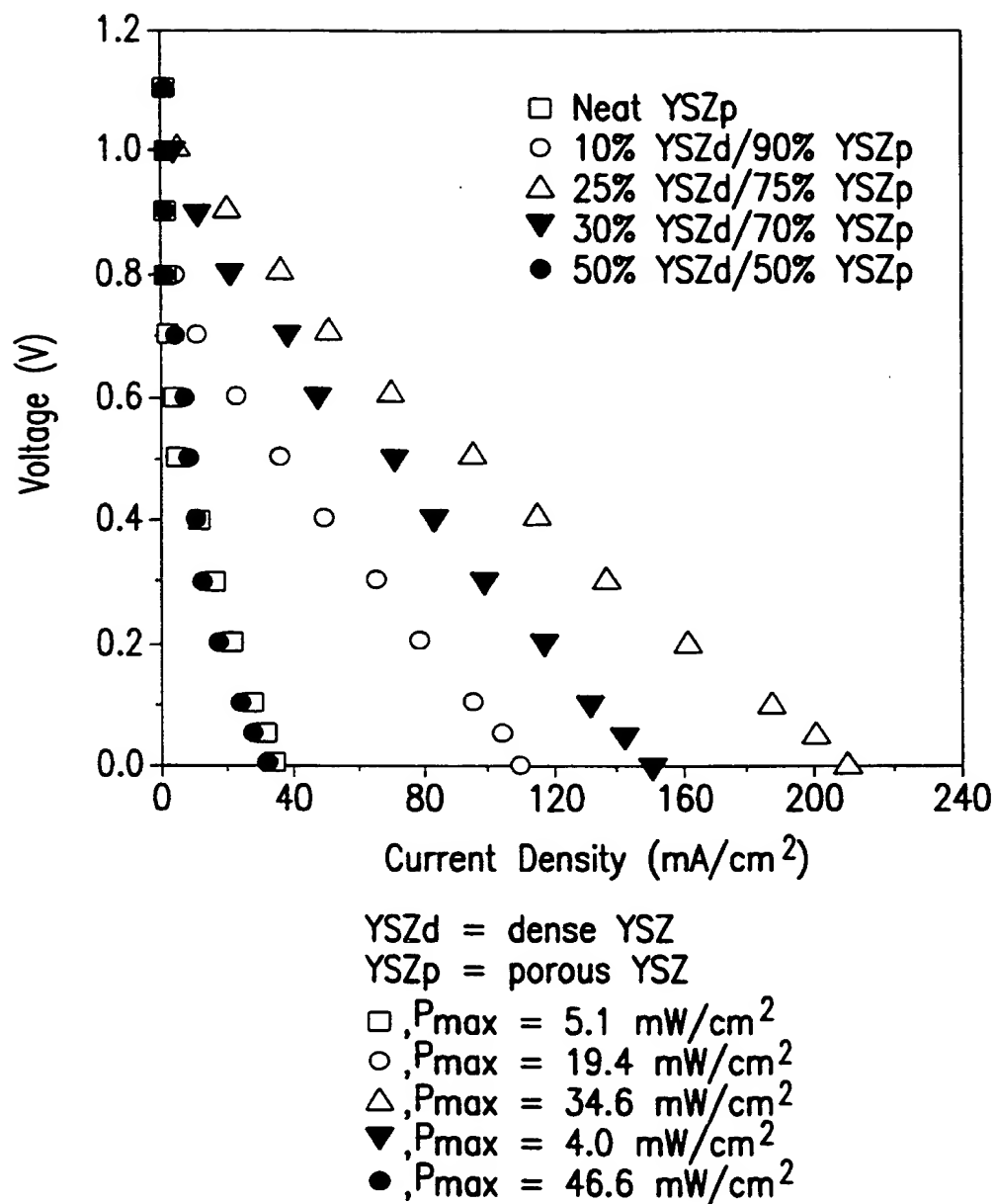


FIG.1

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FIG.2A

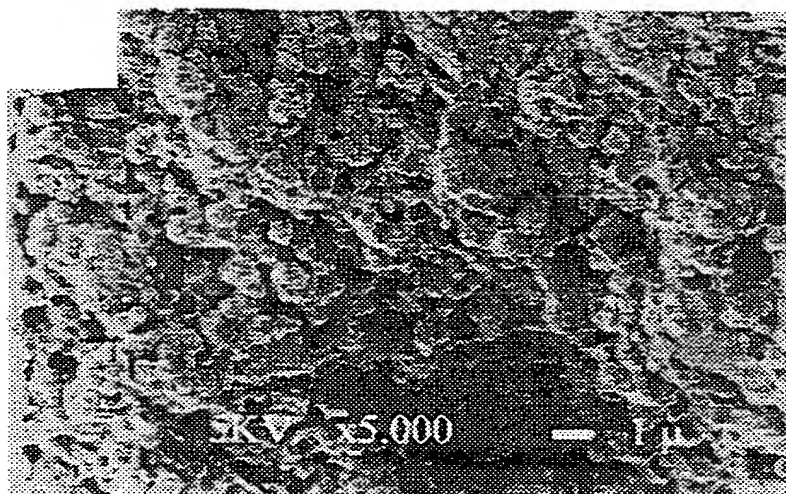


FIG.2B

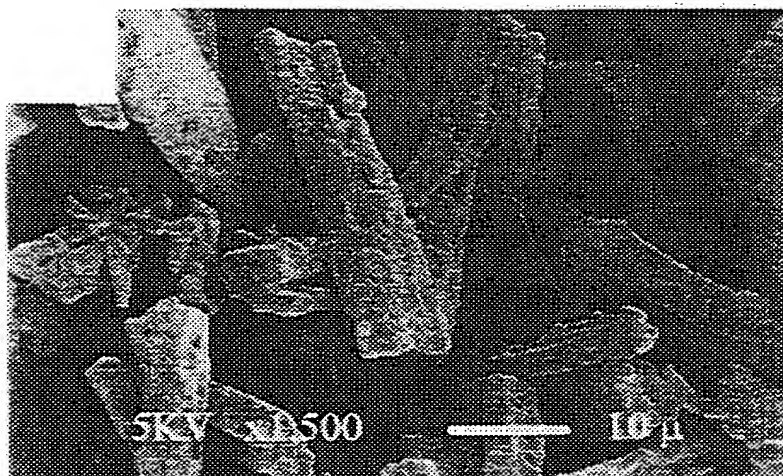
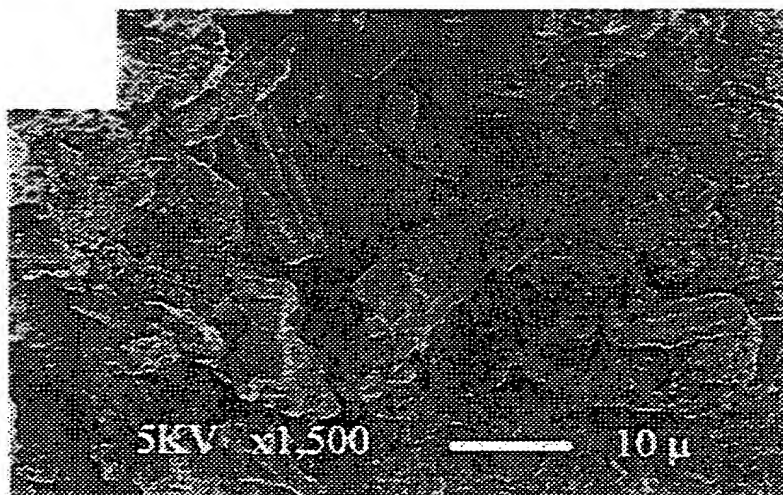


FIG.2C



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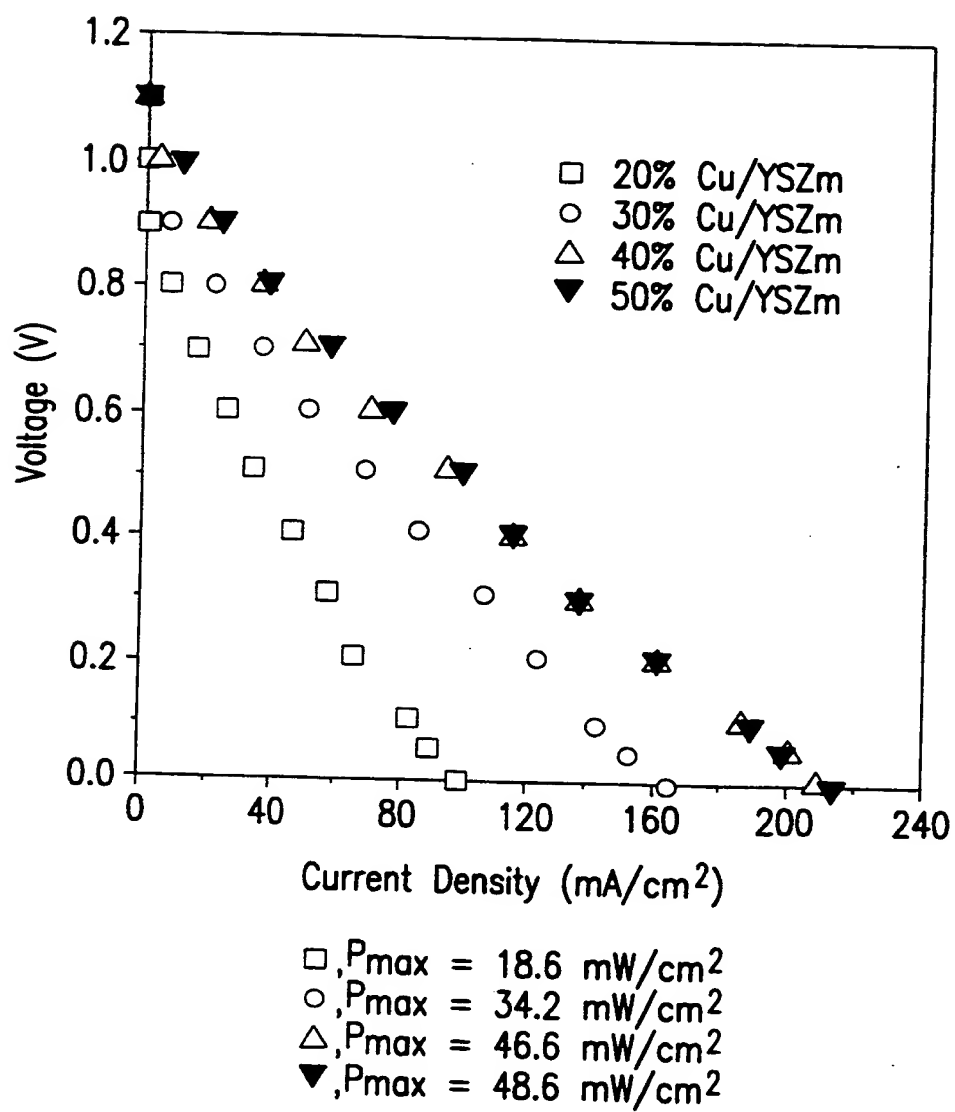


FIG.3

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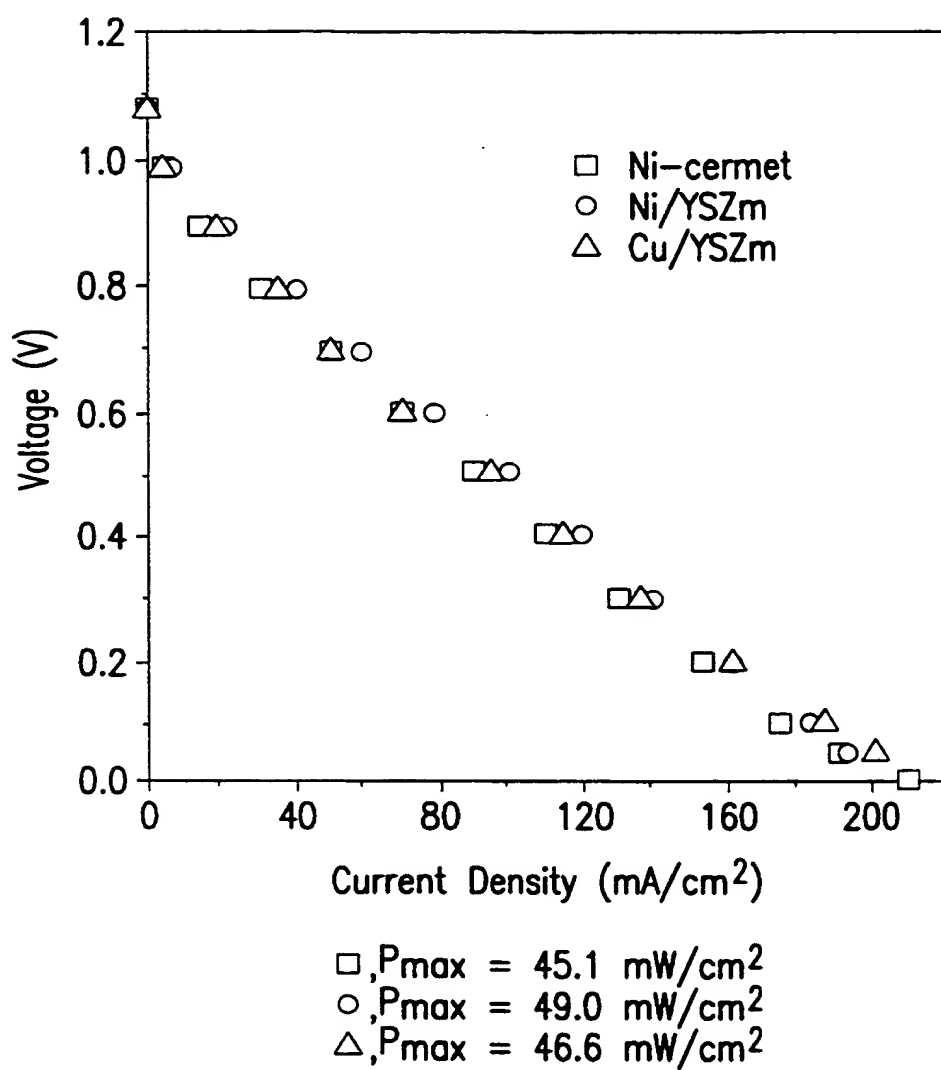


FIG.4

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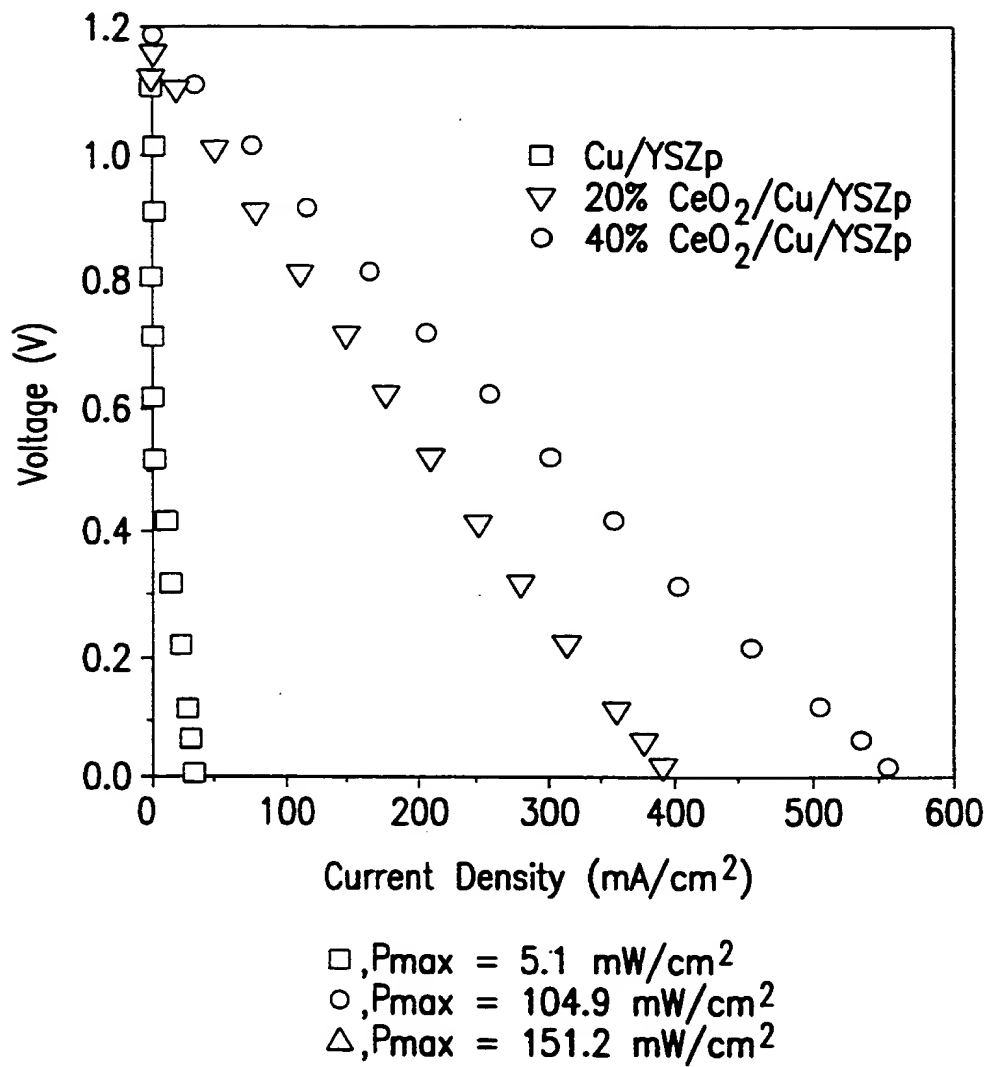


FIG.5

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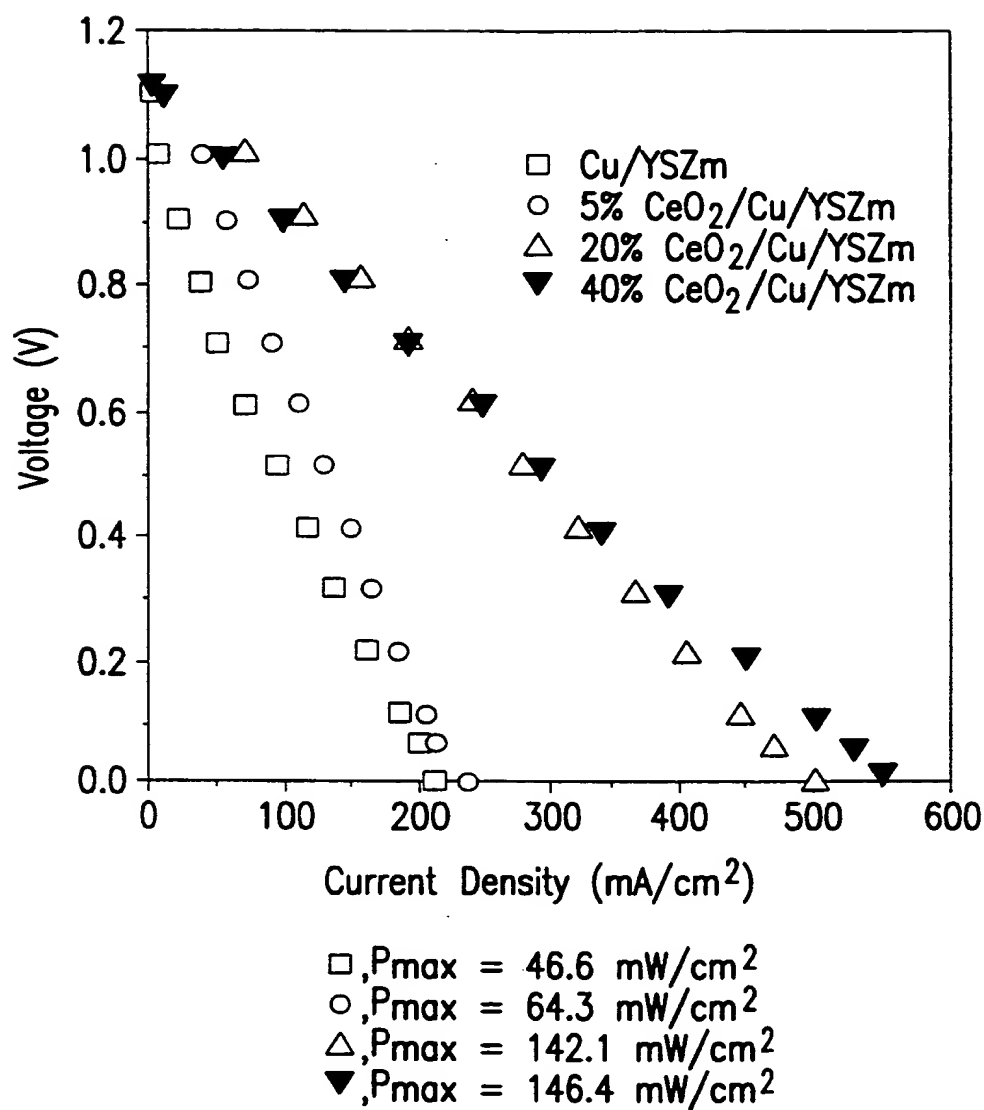


FIG.6

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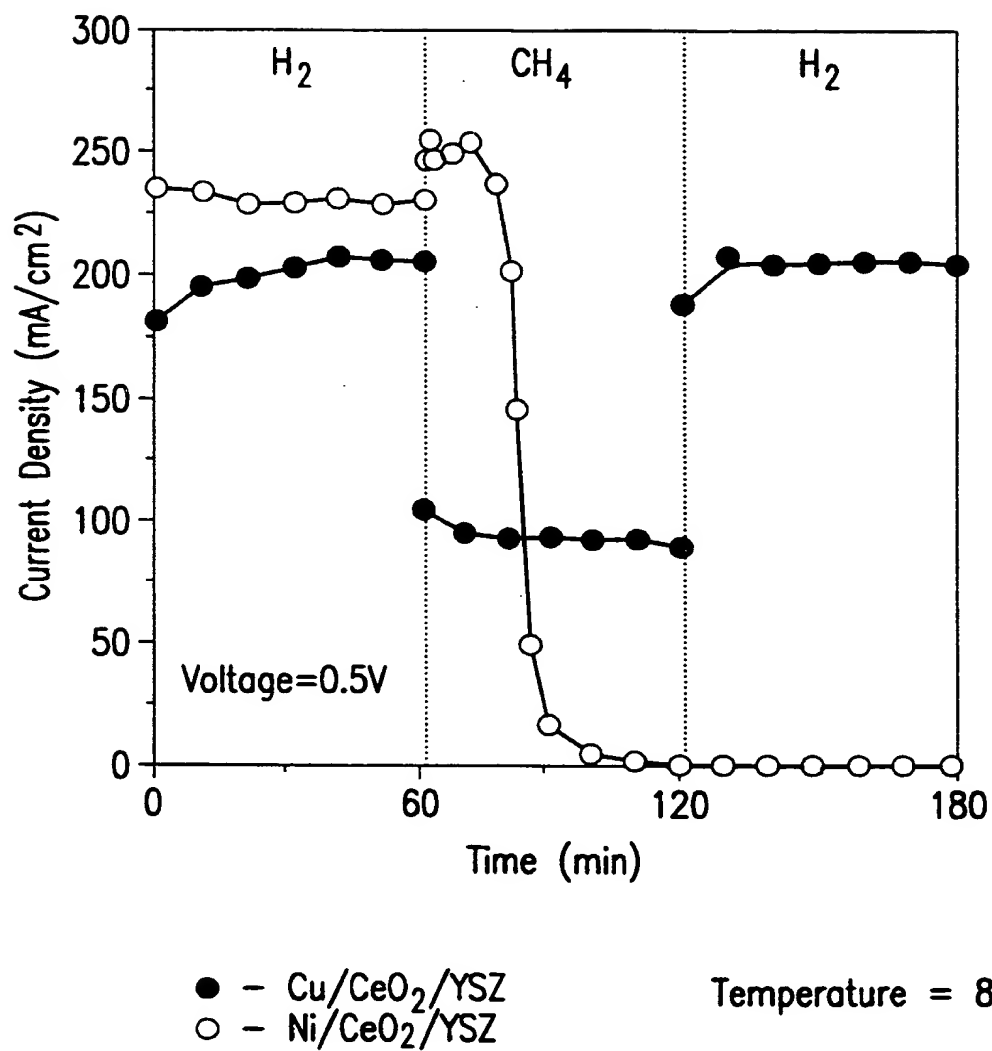


FIG.7

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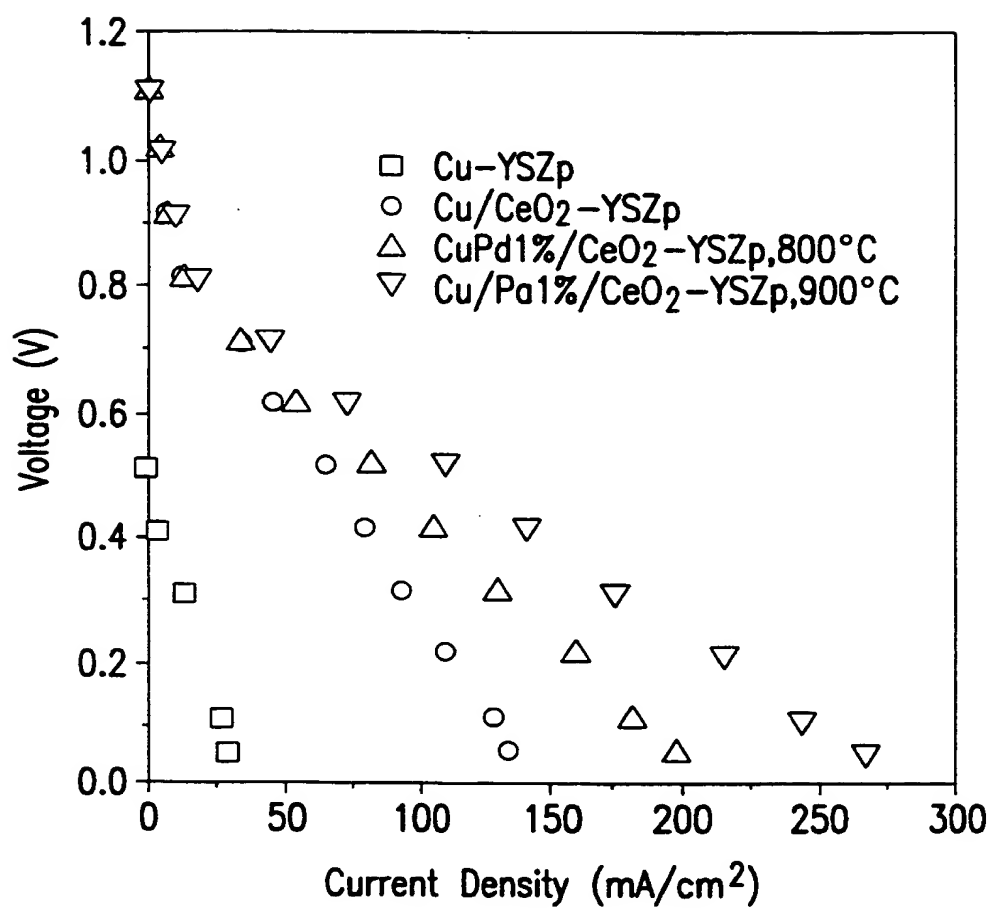


FIG.8



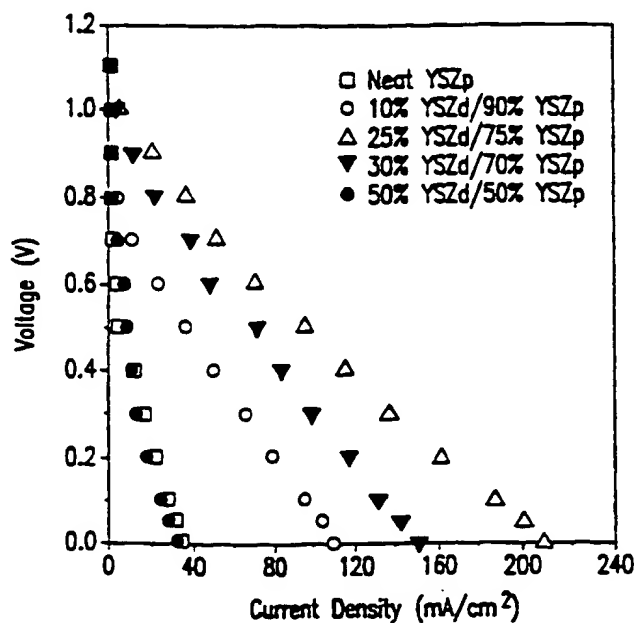
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : H01M 8/12		A1	(11) International Publication Number: WO 00/52780
			(43) International Publication Date: 8 September 2000 (08.09.00)
(21) International Application Number: PCT/US00/05735		(74) Agents: FEJER, Mark, E. et al.; Pauley Petersen Kinne & Fejer, Suite 365, 2800 West Higgins Road, Hoffman Estates, IL 60195 (US).	
(22) International Filing Date: 3 March 2000 (03.03.00)			
(9) Priority Data: 09/261,324 3 March 1999 (03.03.99) US		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/261,324 (CIP) Filed on 3 March 1999 (03.03.99)		Published With international search report. With amended claims and statement.	
(71) Applicant (for all designated States except US): GAS RESEARCH INSTITUTE [US/US]; 8600 West Bryn Mawr Avenue, Chicago, IL 60631 (US).		Date of publication of the amended claims and statement: 16 November 2000 (16.11.00)	
(72) Inventors; and (75) Inventors/Applicants (for US only): GORTE, Raymond, J. [US/US]; 512 Broad Acres Road, Narberth, PA 19072 (US). VOHS, John, M. [US/US]; 45 Sawgrass Lane, Newtown Square, PA 19073 (US). CRACUN, Radu [US/US]; 3426 Bailey Creek Cove, South Collierville, TN 38109 (US).			

(54) Title: METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

(57) Abstract

A method for preparation of an anode for a solid oxide fuel cell in which a plurality of zircon fibers are mixed with a yttria-stabilized zirconia (YSZ) powder, forming a fiber/powder mixture. The fiber/powder mixture is formed into a porous YSZ layer and calcined. The calcined porous YSZ layer is then impregnated with a metal-containing salt solution. Preferred metals are Cu and Ni. An anode and a method for manufacturing a fuel cell containing such anode is also disclosed. Such anode is particularly performant when the fuel cell is fed with dry hydrocarbons, in absence or low content of steam.



YSZd = dense YSZ
 YSZp = porous YSZ

□, $P_{max} = 5.1 \text{ mW/cm}^2$
 ○, $P_{max} = 19.4 \text{ mW/cm}^2$
 △, $P_{max} = 34.6 \text{ mW/cm}^2$
 ▼, $P_{max} = 4.0 \text{ mW/cm}^2$
 ●, $P_{max} = 15.5 \text{ mW/cm}^2$

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31 AUGUST 2001

AMENDED CLAIMS

[received by the International Bureau on 25 September 2000 (25.09.00);
original claims 1, 11, 15 and 20 amended;
original claims 3, 12, 16 and 22 cancelled;
remaining claims unchanged (4 pages)]

1. A method for preparation of an anode for a solid oxide fuel cell comprising the steps of:
 - mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;
 - forming said porous matrix material/powder mixture into a porous YSZ layer;
 - calcining said porous YSZ layer; and
 - impregnating said porous YSZ layer with a Cu-containing salt solution.
2. A method in accordance with Claim 1, wherein said porous matrix material comprises a plurality of zircon fibers.
4. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is mixed with glycerol and applied to an anode side of a YSZ electrolyte, forming said porous YSZ layer on said anode side of YSZ electrolyte.
5. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is added to a tapecast and said tapecast is deposited onto an anode side of a YSZ electrolyte layer, forming said porous YSZ layer on said anode side of YSZ electrolyte.
6. A method in accordance with Claim 5, wherein a cathode is applied to a cathode side of said YSZ electrolyte layer after said calcining of said porous YSZ layer.
7. A method in accordance with Claim 1, wherein a metal content of said porous YSZ layer is at least about 35% by weight of said porous YSZ layer.
8. A method in accordance with Claim 1, wherein said impregnated porous YSZ layer is calcined.

9. A method in accordance with Claim 1, wherein said porous YSZ layer is impregnated with ceria.

10. A method in accordance with Claim 9, wherein said ceria constitutes in a range of about 5% to about 40% by weight of said porous YSZ layer.

11. A method for producing a solid oxide fuel cell comprising the steps of:

mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;

mixing said porous matrix material/powder mixture with glycerol, forming a slurry;

applying said slurry to an anode-facing face of a dense YSZ electrolyte layer, forming a porous anode layer/electrolyte layer assembly;

calcining said porous anode layer/electrolyte layer assembly;

applying a cathode layer to a cathode-facing face of said electrolyte layer, forming a fuel cell assembly;

impregnating said porous anode layer with a Cu-containing salt solution; and calcining said impregnated porous anode layer.

13. A method in accordance with Claim 12, wherein a metal content of said calcined impregnated porous anode layer is at least about 35% by weight of said calcined impregnated porous anode layer.

14. A method in accordance with Claim 11, wherein said porous matrix material comprises a plurality of zircon fibers.

15. In a solid oxide fuel cell comprising an anode electrode, a cathode electrode and an electrolyte disposed between said anode electrode and said cathode electrode, the improvement comprising:

said anode electrode comprising a porous YSZ layer and one of a Cu metal and a Cu alloy.

17. A solid oxide fuel cell in accordance with Claim 15, wherein said anode electrode further comprises ceria.

18. A solid oxide fuel cell in accordance with Claim 15, wherein a metal content of said anode electrode is at least about 35% by weight of said porous YSZ layer.

19. A solid oxide fuel cell in accordance with Claim 17, wherein a ceria content of said anode electrode is in a range of about 5% to 40% by weight of said porous YSZ layer.

20. A method for generating electricity comprising the steps of:
introducing at least one of a hydrocarbon and a carbonaceous fuel directly into an anode side of a solid oxide fuel cell comprising an anode electrode comprising a porous YSZ layer and one of a Cu metal and a Cu alloy, a cathode electrode and an electrolyte disposed between said anode electrode and said cathode electrode;

introducing an oxidant into a cathode side of said solid oxide fuel cell; and
directly oxidizing said at least one of said hydrocarbon and said carbonaceous fuel in said solid oxide fuel cell, resulting in generation of electricity.

21. A method in accordance with Claim 20, wherein said hydrocarbon comprises at least two carbon atoms.

23. A method in accordance with Claim 20, wherein said anode electrode further comprises ceria.

24. A method in accordance with Claim 20, wherein said carbonaceous fuel is an alcohol.

STATEMENT UNDER ARTICLE 19(1)

Claims 2, 4-10, 13, 14, 17-19, 21, 23 and 24 remain the same as originally filed. Applicants are submitting replacement pages 10-13. Original Claim 1 has been deleted and replaced with new Claim 1; original Claim 11 has been deleted and replaced with new Claim 11; original Claim 15 has been deleted and replaced with new Claim 15; and original Claim 20 has been deleted and replaced with new Claim 20. Original Claims 3, 12, 16 and 22 have been deleted.

Claims 1 and 9 have been amended to provide that the porous anode layer is impregnated with a Cu-containing salt solution. Claims 15 and 20 have been amended to provide that the anode electrode comprises a Cu metal or Cu alloy.

Applicants respectfully urge that this amendment of the claims is fully supported by the application as originally filed and, thus, incorporates no new subject matter into the application.

al

Copy for the Elected Office (EO/US)

PCT/US00/05735

INTERNATIONAL COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 05 December 2000 (05.12.00)
Applicant's or agent's file reference GRI-98024PCT
International application No. PCT/US00/05735

IMPORTANT NOTIFICATION
International filing date (day/month/year) 03 March 2000 (03.03.00)

00914638 12204

1. The following indications appeared on record concerning: <input checked="" type="checkbox"/> the applicant <input checked="" type="checkbox"/> the inventor <input type="checkbox"/> the agent <input type="checkbox"/> the common representative		
Name and Address CRACIUN, Radu 3426 Bailey Creek Cove South Collierville, TN 38109 United States of America	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning: <input type="checkbox"/> the person <input type="checkbox"/> the name <input type="checkbox"/> the address <input checked="" type="checkbox"/> the nationality <input type="checkbox"/> the residence		
Name and Address CRACIUN, Radu 3426 Bailey Creek Cove South Collierville, TN 38109 United States of America	State of Nationality RO	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary:		
4. A copy of this notification has been sent to: <input checked="" type="checkbox"/> the receiving Office <input type="checkbox"/> the designated Offices concerned <input type="checkbox"/> the International Searching Authority <input checked="" type="checkbox"/> the elected Offices concerned <input checked="" type="checkbox"/> the International Preliminary Examining Authority <input type="checkbox"/> other:		

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740 14.35	Authorized officer Maria Victoria CORTIELLO Telephone No.: (41-22) 338.83.38
---	--

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year)

24 September 2001 (24.09.01)

Applicant's or agent's file reference

GRI-98024PCT

IMPORTANT NOTIFICATION

International application No.

PCT/US00/05735

International filing date (day/month/year)

03 March 2000 (03.03.00)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

GAS RESEARCH INSTITUTE
8600 West Bryn Mawr Avenue
Chicago, IL 60631
United States of America

State of Nationality

US

State of Residence

US

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

THE TRUSTEES OF THE UNIVERSITY OF
PENNSYLVANIA
3700 Market Street
Suite 300
Philadelphia, PA 19104-3147
United States of America

State of Nationality

US

State of Residence

US

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☐ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Ning XU

Facsimile No.: (41-22) 740.14.35

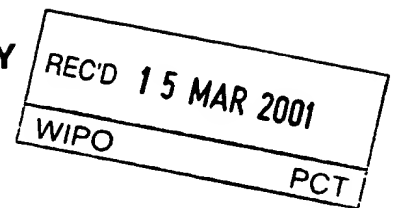
Telephone No.: (41-22) 338.83.38

091914688

REPLACED BY
ART 34 AMDT

PATENT COOPERATION TREATY

PCT



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference GRI-98024PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/05735	International filing date (day/month/year) 03/03/2000	Priority date (day/month/year) 03/03/1999
International Patent Classification (IPC) or national classification and IPC H01M8/12		
Applicant GAS RESEARCH INSTITUTE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03/10/2000	Date of completion of this report 16.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Battistig, M Telephone No. +31 70 340 3738 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/05735

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-9 as originally filed

Claims, No.:

1-24 with telefax of 05/10/2000

Drawings, sheets:

1/8-8/8 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/05735

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-24
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-24
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-24
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US00/05735

AD V:

Novelty:

A fuel cell anode comprising a porous YSZ layer and one of a Cu metal or a Cu alloy and the method for manufacturing it has not been disclosed in any cited prior art document. The subject-matter of claims 1 to 24 is novel.

Inventive step:

Document US5543239 (D1), which is considered to represent the closest prior art, describes a fuel cell having an anode made by mixing NiO powder and YSZ powder and then firing it. The ceramic obtained is then reduced in H₂ to an anode material consisting of Ni and YSZ (see example 1(a)).

Document US5656387 (D2) is also considered to represent the closest prior art, and describes an anode formed by DC reactive magnetron sputtering, containing 68.8% Ni and 26.6 % Zr and 4.53% Y (see claims 1 to 5).

The problem is how to provide an alternative YSZ - Metal anode containing another metal than Ni.

It is not obvious for the skilled person, when starting from D1 or D2, to replace Ni by Cu and arrive at the invention, because it has not been suggested anywhere in the prior art, nor it is common knowledge in the field.

The subject-matter of claims 1 to 24 do appear to involve an inventive step.

ADVII:

Clarity (Art. 6 PCT):

In the new set of claims submitted on 05-10-2000, claims 3, ~~12, 16~~, 22 are missing, because they have been deleted. The new set of claims should be renumbered.

WE CLAIM:

1. A method for preparation of an anode for a solid oxide fuel cell comprising the steps of:

5 mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;

forming said porous matrix material/powder mixture into a porous YSZ layer; calcining said porous YSZ layer; and

impregnating said porous YSZ layer with a metal-containing salt solution.

10 2. A method in accordance with Claim 1, wherein said porous matrix material comprises a plurality of zircon fibers.

15 3. A method in accordance with Claim 1, wherein said metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

20 4. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is mixed with glycerol and applied to an anode side of a YSZ electrolyte, forming said porous YSZ layer on said anode side of YSZ electrolyte.

25 5. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is added to a tapecast and said tapecast is deposited onto an anode side of a YSZ electrolyte layer, forming said porous YSZ layer on said anode side of YSZ electrolyte.

6. A method in accordance with Claim 5, wherein a cathode is applied to a cathode side of said YSZ electrolyte layer after said calcining of said porous YSZ layer.

30 7. A method in accordance with Claim 1, wherein a metal content of said porous YSZ layer is at least about 35% by weight of said porous YSZ layer.

8. A method in accordance with Claim 1, wherein said impregnated porous YSZ layer is calcined.

5 9. A method in accordance with Claim 1, wherein said porous YSZ layer is impregnated with ceria.

10 10. A method in accordance with Claim 9, wherein said ceria constitutes in a range of about 5% to about 40% by weight of said porous YSZ layer.

10 11. A method for producing a solid oxide fuel cell comprising the steps of:

mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;

15 mixing said porous matrix material/powder mixture with glycerol, forming a slurry;

applying said slurry to an anode-facing face of a dense YSZ electrolyte layer, forming a porous anode layer/electrolyte layer assembly;

calcining said porous anode layer/electrolyte layer assembly;

20 applying a cathode layer to a cathode-facing face of said electrolyte layer, forming a fuel cell assembly;

impregnating said porous anode layer with a metal-containing salt solution; and

calcining said impregnated porous anode layer.

25 12. A method in accordance with Claim 11, wherein said metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

13. A method in accordance with Claim 12, wherein a metal content of said calcined impregnated porous anode layer is at least about 35% by weight of said calcined impregnated porous anode layer.

5 14. A method in accordance with Claim 11, wherein said porous matrix material comprises a plurality of zircon fibers.

15. In a solid oxide fuel cell comprising an anode electrode, a cathode electrode and an electrolyte disposed between said anode electrode and said cathode electrode, the improvement comprising:

10 said anode electrode comprising a porous YSZ layer and an electron-conducting metal having an oxide form which melts at a temperature less than about 1550°C.

15 16. A solid oxide fuel cell in accordance with Claim 15, wherein said electron-conducting metal is Cu.

17. A solid oxide fuel cell in accordance with Claim 15, wherein said anode electrode further comprises ceria.

20 18. A solid oxide fuel cell in accordance with Claim 15, wherein a metal content of said anode electrode is at least about 35% by weight of said porous YSZ layer.

25 19. A solid oxide fuel cell in accordance with Claim 17, wherein a ceria content of said anode electrode is in a range of about 5% to 40% by weight of said porous YSZ layer.

20. A method for generating electricity comprising the steps of:
introducing at least one of a hydrocarbon and a carbonaceous fuel directly into
an anode side of a solid oxide fuel cell comprising an anode electrode comprising a porous
YSZ layer and an electron-conducting metal having an oxide form which melts at a
5 temperature less than about 1550°C, a cathode electrode and an electrolyte disposed between
said anode electrode and said cathode electrode;

introducing an oxidant into a cathode side of said solid oxide fuel cell; and
directly oxidizing said at least one of said hydrocarbon and said carbonaceous
fuel in said solid oxide fuel cell, resulting in generation of electricity.

10

21. A method in accordance with Claim 20, wherein said hydrocarbon
comprises at least two carbon atoms.

22. A method in accordance with Claim 20, wherein said electron-
conducting metal is Cu.

15

23. A method in accordance with Claim 20, wherein said anode electrode
further comprises ceria.

20

24. A method in accordance with Claim 20, wherein said carbonaceous
fuel is an alcohol.

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

T :

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 26 April 2000 (26.04.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference GRI-98024PCT	International application No. PCT/US00/05735

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

GAS RESEARCH INSTITUTE (for all designated States except US)

GORTE, Raymond, J. et al (for US)

International filing date : 03 March 2000 (03.03.00)

Priority date(s) claimed : 03 March 1999 (03.03.99)

Date of receipt of the record copy
by the International Bureau : 04 April 2000 (04.04.00)

List of designated Offices :

AP : GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW

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31 AUGUST 2001

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:



time limits for entry into the national phase



confirmation of precautionary designations



requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

MVC
Maria Victoria CORTIELLO

Telephone N. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 02 May 2000 (02.05.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference GRI-98024PCT	
International application No. PCT/US00/05735	International filing date (day/month/year) 03 March 2000 (03.03.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 03 March 1999 (03.03.99)
Applicant GAS RESEARCH INSTITUTE et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
03 Marc 1999 (03.03.99)	09/261,324	US	25 Apr 2000 (25.04.00)

EXPRESS MAIL NO. EL 815 472 76805MAILED 31 AUGUST 2001The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Taieb Akremi 

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

T :
FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 08 September 2000 (08.09.00)		
Applicant's or agent's file reference GRI-98024PCT		IMPORTANT NOTICE
International application No. PCT/US00/05735	International filing date (day/month/year) 03 March 2000 (03.03.00)	
Priority date (day/month/year) 03 March 1999 (03.03.99)		
Applicant GAS RESEARCH INSTITUTE et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).
3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
08 September 2000 (08.09.00) under No. WO 00/52780

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

EXPRESS MAIL NO. EL 815 472 76805

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	MAILED Authorized officer <u>31 AUGUST 2001</u> J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference GRI-98024PCT	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/US 00/ 05735	International filing date (day/month/year) 03/03/2000	(Earliest) Priority Date (day/month/year) 03/03/1999
Applicant GAS RESEARCH INSTITUTE et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

EXPRESS MAIL NO. EL815 472 768US

5. With regard to the abstract,

MAILED 31 August 2001

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure N .

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 00/05735

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The abstract has to be changed as follows:

Line 5, add the following part:

"An anode and a method for manufacturing a fuel cell containing such anode is also disclosed. Such anode is particularly performant when the fuel cell is fed with dry hydrocarbons, in absence or low content of steam."

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference GRI-98024PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 00/ 05735	International filing date (day/month/year) 03/03/2000	(Earliest) Priority Date (day/month/year) 03/03/1999
Applicant GAS RESEARCH INSTITUTE et al.		

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This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 00/05735

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The abstract has to be changed as follows:

Line 5, add the following part:

"An anode and a method for manufacturing a fuel cell containing such anode is also disclosed. Such anode is particularly performant when the fuel cell is fed with dry hydrocarbons, in absence or low content of steam."

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/05735

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M8/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	✓ US 5 543 239 A (VIRKAR ANIL V ET AL) 6 August 1996 (1996-08-06) example 1A	15, 18, 20
A	✓ PATENT ABSTRACTS OF JAPAN vol. 013, no. 176 (E-749), 25 April 1989 (1989-04-25) & JP 01 007475 A (MITSUBISHI HEAVY IND LTD), 11 January 1989 (1989-01-11) abstract	1-3, 7, 11-14
X	✓ US 5 656 387 A (BARNETT SCOTT ALEXANDER ET AL) 12 August 1997 (1997-08-12) claims 1-5	15, 18, 20
A	✓ EP 0 338 823 A (TOA NENRYO KOGYO KK) 25 October 1989 (1989-10-25) claims 1-10	1-24

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *"A" document defining the general state of the art which is not considered to be of particular relevance
- *"E" earlier document but published on or after the international filing date
- *"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *"O" document referring to an oral disclosure, use, exhibition or other means
- *"P" document published prior to the international filing date but later than the priority date claimed

*"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*"&" document member of the same patent family

Date of the actual completion of the international search

18 July 2000

Date of mailing of the international search report

25/07/2000

Name and mailing address of the ISA

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Authorized officer

Battistig, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/05735

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5543239	A	06-08-1996	NONE	
JP 01007475	A	11-01-1989	NONE	
US 5656387	A	12-08-1997	NONE	
EP 0338823	A	25-10-1989	JP 2177265 A	10-07-1990
			JP 2037669 A	07-02-1990
			DE 68917192 D	08-09-1994
			DE 68917192 T	17-11-1994
			US 4950562 A	21-08-1990
			JP 2050983 A	20-02-1990
			JP 2604437 B	30-04-1997